



Short communication

Synthesis of the diazonium (perfluoroalkyl) benzenesulfonimide monomer from Nafion monomer for proton exchange membrane fuel cells

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H I G H L I G H T S

- First diazonium (perfluoroalkyl) benzenesulfonimide monomer.
- A new kind of nanoscale material to improve the interface between electrolyte and electrode.
- Detailed characterizations of all intermediates and the final monomer.
- Catalytic reduction nitroaromatics without affect perfluorovinyl ether group.

A R T I C L E I N F O

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One diazonium (perfluoroalkyl) benzenesulfonimide monomer, perfluoro-3, 6-dioxa-4-methyl-7-octene benzenesulfonyl imide, has been synthesized from Nafion monomer for the first time. With trifluorovinyl ether and diazonium precursors, the partially-fluorinated diazonium PFSI monomer can be polymerized and will provide chemically bonding with carbon electrode in proton exchange membrane fuel cells. A systematic study of the synthesis and characterization of this diazonium PFSI monomer has been conducted by varying reaction conditions. The optimized synthesis method has been established in the lab.

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1. Introduction

Lately, the growing interest related to cleaner energy production technologies has promoted the consideration and study of ionomers as proton exchange membrane (PEM) in fuel cells. Due to electrochemical stability requirements, perfluorinated materials have been preferred as the best candidates for satisfying the needs for the system. Achieving stable, highly proton conducting and cost-effective polymer membrane of PEM fuel cells attracts considerable interest [1]. (Perfluoroalkyl) Benzenesulfonimide

(PFSI) polymers are proposed to replace perfluoroalkyl sulfonic acid (PFSA) polymers, such as Nafion, for PEM fuel cells [2]. For PEM fuel cells' three phase reaction system, such as active layer in Membrane Electrolyte Assembly (MEA), a stable interface between the electrolyte and the carbon electrodes has to be maintained so that the number of reaction sites remains as high as possible for long operation times [3]. As the potential route to improve their interface, exploratory research to develop a new family of nanoscale materials has begun. The goal is to maximize the activity of catalyst particles in contact with PEM fuel cell electrodes. Fig. 1 shows the overall structure that we have envisaged for the proposed materials. The top one is conventional electrode fabricated using Pt-decorated carbon powder and polymer electrolyte, such as Nafion®; the bottom one is proposed electrode based on carbon aerogel with interior pores decorated with Pt particles and grafted electrolyte. Chemically attaching the perfluoroalkyl pendant of

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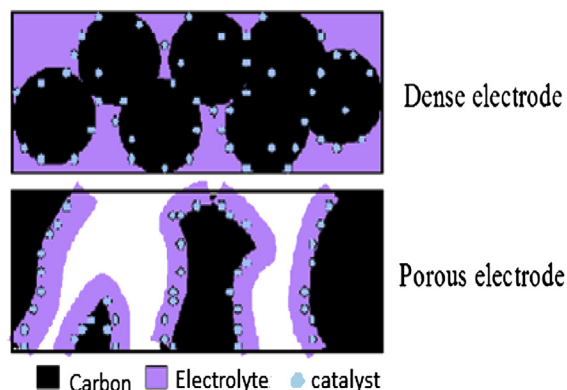


Fig. 1. Nanoporous carbon/catalyst/electrolyte fuel cell electrodes.

electrolyte onto the electrode can dramatically influence the stability, conductivity, and catalyst efficiency of PEM fuel cells (Fig. 1) [4]. Additionally, diazonium compounds are often reported to modify the carbon materials for various applications [5]. In particular, the preparation and characterization for some diazonium PFSI zwitterions, as small molecules, was completed and reported earlier [6]. One of these zwitterions was investigated by Dr. Creager and the first author of this paper for electrochemically attaching to glassy carbon materials. Fig. 2 illustrates the reductive electrochemical method to graft the aryl fluoro-sulfonimide diazonium zwitterion onto glassy carbon to produce a robust bonded fluorosulfonimide electrolyte [7].

Recently, Salguero, Sherman, and Liu patent their results about preparing some amino aryl perfluorinated sulfonic acid precursors and in situ attaching them to the carbon substrate [8]. The PFSA ionomers reported with small molecular weight are used for the precursors. PFSI polymers, on the other hand, are known with great thermal stability in the acid form, better electrochemical inertness, and possibly less susceptibility to dehydration and oxidative degradation than PFSA polymers [9]. Therefore, it would be more interesting to chemically bond PFSI polymers, instead of PFSA polymers, onto carbon substrate in PEM fuel cells. The designed diazonium PFSI monomer will provide this possibility. After the facile loss of N_2 , a carbon–carbon covalent bond is formed between the aromatic group and the carbon electrode. This chemical bonding can be completed via electroreduction or thermal decomposition of diazonium group. [10] With the similar functional group (diazonium group) as small diazonium zwitterions, the new monomer is expected to work likely as binding material in electrode.

We thus elected to prepare this particular diazonium PFSI monomer (the structure shown in Fig. 3). The monomer contains Nafion monomer's basic perfluoroalkyl chain structure with

perfluorovinyl ether groups, which can be copolymerized with tetrafluorovinyl ether and provide excellent thermal and mechanic stability. Moreover, the perfluorosulfonic acid ($-SO_3H$) is replaced with stronger acid, perfluorosulfonimide ($-SO_2NHSO_2-$), for better proton conductivity. The similar PFSI polymers' synthesis from Nafion monomer was reported before [11].

Therefore, the monomer discussed in this paper will be the one that contains diazonium aromatic group, which balances the sulfonamide group as the first zwitterionic monomer.

Synthesis of the diazonium PFSI monomers indicate that they can offer the membrane structure variations and increase the ability for PEM fuel cell operations under more extreme conditions with better structural properties as well as the intimate chemical attachment to the carbon electrodes [12].

2. Results and discussion

2.1. Preparation summary

Due to the diazonium functional group, perfluorovinyl ether group, and the perfluoroalkyl sulfonimide group, the monomer's reactivity is a critical concern to design the synthesis routes. The synthesis routes to access this particular monomer can be summarized in six steps: (1) an ammonolysis reaction, (2) a bromination reaction, (3) a coupling reaction, (4) a reduction reaction, (5) a debromination reaction, and (6) a diazotization reaction.

2.2. Synthesis discussion and optimization

The first step (step i in Scheme 1) is the ammonolysis of aryl sulfonyl chloride to afford the aryl sulfonamide by treating with an excess of aqueous ammonia (a.k.a. ammonium hydroxide) or liquid ammonia. The stoichiometry requires two moles of ammonia per mole of the sulfonyl chloride, resulting that the "Cl" atom is replaced by the " $-NH_2$ " group and the formation of "HCl" is neutralized by some of the excess ammonia. Both the organic reactant and the organic product are insoluble in water and it is difficult to determine if the reaction is occurring and when it is completed. It is a typical S_N2 reaction. The side product is NH_4Cl . The by-product is formed from the hydrolysis of the "sulfonyl chloride" in aqueous medium. Since NH_3 is a better nucleophile than H_2O and the ammonolysis prevails over hydrolysis. Any of the "sulfonic acid" formed by hydrolysis will be converted to the water soluble ammonium salt. Pure *p*-nitrobenzenesulfonylamide **2** was isolated by vacuum filtration from water since both the hydrolysis by-product and side-product NH_4Cl are completely soluble in water.

Because of perfluoroalkyl group as the strong electron withdrawing group, no addition reaction occurs for Nafion monomer at acid condition and basic condition at room temperature. But directly coupling Nafion monomer and the aryl sulfonamide was unsuccessful, presumably due to the reactivity of the perfluorovinyl ether group toward basic medium at high temperature. Therefore, the monomer's perfluorovinyl ether double bond is protected with Br_2 before the coupling reaction (step ii in Scheme 1) [13].

Electron poor brominated Nafion monomer is prone to S_N2 -type reaction (step iii in Scheme 1) not only with aryl sulfonamide but also with weak nucleophile basic water at high temperature. The

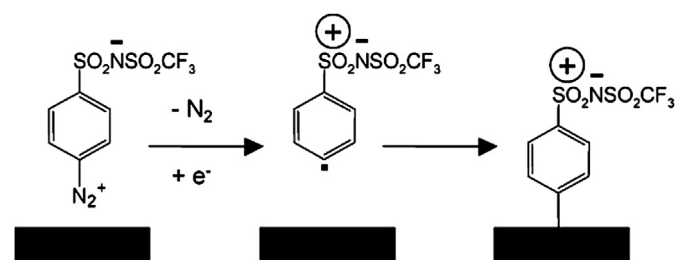


Fig. 2. Reductive electrochemical grafting of an aryl fluoro-sulfonimide diazonium zwitterion onto glassy carbon.

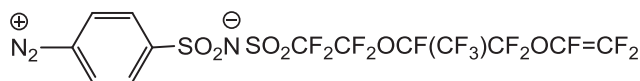
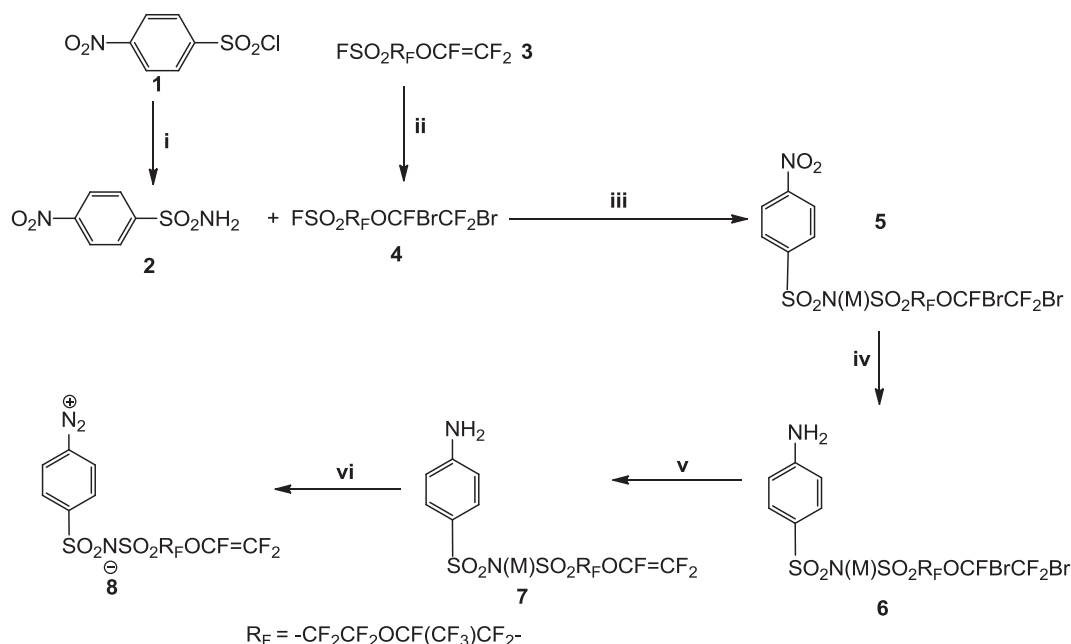


Fig. 3. Structure of first diazonium PFSI monomer.



Scheme 1. Synthesis route for the diazonium PFSI monomer (step i: ammonia water, reflux at 100 °C overnight, 80%; or $NH_3(l)$, –50 °C to r.t., 95%; step ii: Br_2 , 0 °C to r.t., 70%; step iii: *N,N*-diisopropylethylamine, dry CH_3CN , 80 °C, 85%; step iv: hydrogen gas, iron powder, sonication, dry CH_3CN , r.t., 75%; step v: zinc powder, HCl, dry CH_3CN , 80 °C, 78%; step vi: HCl, $NaNO_2$, 0 °C, 45%).

sticky DIEA associated crude product is hard to purify. The purification requires column chromatography separation and recrystallization as Cs salts after acidification. The optimized methods for the coupling reaction to remove inseparable hydrolysis side product include: 1) carrying the reaction at dry condition with all dry reagents or 2) employing extra amount of brominated Nafion monomer. However, the ^{19}F NMR spectra showed two peaks for CF_2 (**a** and **a'** in Fig. 4) at δ –115 and –117 ppm, which had the total integration around 2. The first hypothesis is that one peak belongs to the hydrolysis of the DIEA salts of brominated Nafion monomer (Fig. 5). Sticky imine salts are usually hard to remove by simple extraction. An extra experiment, directly reacting brominated Nafion monomer with moist DIEA was performed to yield the hydrolysis compound (Fig. 5). According to ^{19}F NMR, it did not match the extra peak at 117 ppm. The other possibility is that the two fluorine atoms are diastereotopic fluorine atoms (Fig. 4). The fluorine **a** and **a'** have little difference in chemical shift. These two fluorine peaks keep showing up in all fluorine spectra of intermediate and product, and the total integration is always around 2 for two fluorine atoms.

Next reduction of nitro aromatic compound was examined. The optimized reaction condition (step iv in Scheme 1) was established as sonication of aromatic nitro compound with Fe/HCl/ H_2 at room temperature. The other reducing reagents, including tin (II) chloride/HCl [14], sodium polysulfide [15] and iron/HCl or iron/acetic acid [16], were not successful, either not working in basic condition or having the inorganic impurities. Also, the temperature is critical for the reaction. Simply letting

solution refluxed at high temperature with Fe/HCl/ H_2 as the reduce approach for other regular aromatic nitro compound will bring the side reaction. The reason is that the debromination of brominated perfluorovinyl ether will be prone to occur at high temperature. The converted double bond will be hydrohalogenated subsequently. Therefore, the use of iron/HCl/ H_2 in ultrasound sonicator at room temperature leads to the formation of corresponding aromatic amine. The product supposedly is *p*- NH_2 -PhSO $_2$ NHSO $_2$ Rf (Rf = $CF_2CF_2OCF(CF_3)CF_2OCFBrCF_2Br$). Similar to aniline, the characterization of the reduce product depends on acidic vs. basic conditions. The perfluorosulfonimide group is very acidic and can protonate the primary amine on the aromatic ring with the structure as **6**, *p*- NH_3^+ -PhSO $_2$ N $^-$ SO $_2$ Rf. Basifying the product with 10% NaOH can afford the primary amine, but also deprotonate the sulfonimide. When this occurred, the primary amine peak shifted from 3000 cm^{-1} to the left at around 3400 cm^{-1} . The chemical shifts of para aromatic protons moved from at δ 8.01 and 7.59 ppm to the right at δ 7.58 ppm and δ 6.63 ppm in 1H NMR.

Debromination was promoted (step v in Scheme 1) next with activated Zinc in polar solvent acetonitrile with around 70% yield. TLC cannot be used to monitor reaction since the polarity of debromination product is very similar to its reactant. The ^{19}F NMR spectrum proved that the double bond was reproduced after the reaction. The diazonium PFSI monomer (step vi in Scheme 1) was finally prepared through diazotization with $NaNO_2$ /HCl for 2 h. And the brown product was purified with vacuum filtration in a yield around 60%.

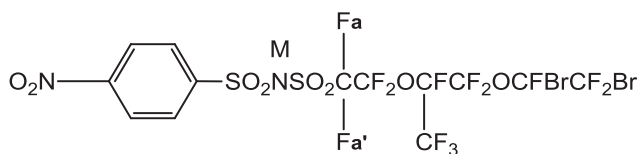


Fig. 4. Structure of coupling product **5**.

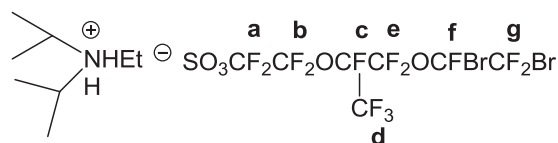


Fig. 5. Possible hydrolysis by-product from coupling reaction.

3. Conclusions

In summary, we report the first synthesis and characterizations of diazonium PFSI monomer. The synthesis route was optimized. We are currently developing methods to various aromatic derivatives, which will be reported in due course. The analogues of monomers will be collected to compare the properties and polymerized later for PEM fuel cell applications.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jpowsour.2013.10.024>.

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